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Mercury Transportation in Soil Using Gypsum from Flue Gas Desulphurization Unit in Coal-Fired Power Plant

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MECURY TRANSPORTATION IN SOIL USING GYPSUM FROM FLUE GAS DESULPHURIZATION UNIT IN COAL-FIRED POWER PLANT

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MECURY TRANSPORTATION IN SOIL USING GYPSUM FROM FLUE GAS DESULPHURIZATION UNIT IN COAL-FIRED POWER PLANT

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This work investigates mercury flux in soil amended by gypsum from flue gas desulphurization (FGD) units of coal-fired power plants. There are two phases of this research, including field and greenhouse studies. Previous studies indicate that FGD gypsum could increase corn yield, but may lead to more mercury uptake by corn.

Recent studies have been carried out in greenhouses to investigate mercury transport in FGD gypsum treated soil. Major aspects include uptake of mercury by plants and emission of mercury into the atmosphere based on application rates of FGD gypsum. Additional aspects include rainfall, temperature, soil, and plants types. Higher FGD gypsum application rates generally led to higher mercury concentration in the soil, as well as, increased mercury emission into the atmosphere, and increased mercury levels in plants, especially roots and leaves. Soil properties and plant species also played important roles in mercury transport. In addition, it was also found that increased water and higher temperatures may contribute to mercury emission in the atmosphere.

Some plants, such as tall fescue, were able to prevent mercury from atmospheric emission and infiltration within the soil. Mercury concentration in the stem of plants was found to be increased and then plateaued upon increasing FGD gypsum application. However, mercury in roots and leaves was generally increased upon increasing FGD gypsum application rates. Some mercury was likely absorbed by leaves of plants from mercury in the surrounding atmosphere.

1. Introduction

1.1 Background

Coal is a major fossil fuel, which is burned to produce electricity and heat. Approximately half of U.S. electricity, 45% electricity in 2010, is generated from coal.[1] However, coal combustion leads to many environmental pollutant issues, such as acid rain, greenhouse gases, and heavy metals. In 1990, the U.S. Clean Air Act enacted regulations on sulfur dioxide emissions from coal combustion. This law forced coal-fired power plants to install flue gas desulphurization (FGD) scrubbers to decrease the sulfur content in flue gas.

Generally, the high sulfur content in coal is emitted during coal combustion and simultaneously generates a large amount of FGD gypsum. According to the report of American Coal Ash Association (ACAA), approximately 33 million metric tons of FGD gypsum was produced in 2007[2]. Kentucky is a major coal producing state and installs more FGD scrubber systems than most other states in the nation. Therefore, FGD by-products that are produced in Kentucky have lead to pressure for recycling of gypsum from coal-fired power plants. Currently, FGD gypsum is used for wallboard production and as a raw material for cement production. In recent years, FGD gypsum has been used in agriculture on a limited basis to improve soil quality and increase soil nutrients. However, concerns about the release of hazardous elements, especially mercury, have inhibited this beneficial recycling method. Mercury in FGD gypsum amended soil may evaporate into the atmosphere, infiltrate into underground water, and be absorbed by plants. Therefore, mercury transportation behavior in FGD gypsum amended soil was of

interest to agriculture. The purpose of this study was to investigate the mercury transport from FGD gypsum treated soil.

1.2 Generation of Flue Gas Desulphurization Gypsum

After coal combustion in the boiler, the flue gas (mixture of N_2, unreacted O_2, H_2O, CO_2, SO_2, and NO_x) passes through the Selective Catalytic Reduction (SCR) at 400℃. SCR uses catalyst to reduce nitrogen oxides (NO_x) into nitrogen and water. The active constituent of the catalyst is a metal oxide supported by ceramic materials, such as titanium oxide. The metal oxides are vanadium, molybdenum and tungsten oxides.

The flue gases then enter the Air Pre-Heater (APH) to cool the flue gas from 400℃ to 175℃, while simultaneously pre-heating the air for combustion to greater than 250℃.

The cooled flue gas enters the Electrostatic Precipitator (ESP) at 175℃ and/or the baghouse to collect particles from the flue gas. ESP collects the particles using a pulsating electrostatic charge. The bag house collects the particles in a filter.

The flue gas is subsequently routed into the Flue Gas Desulphurization (FGD) scrubber to decrease SO_2 in the flue gas at around 110℃. The product of the FGD scrubber is FGD gypsum. There are wet and dry scrubbers. In the wet scrubber, crushed lime or limestone is used as the reagent. Before reacting with SO_2, lime and limestone are mixed with water and then sprayed from the top of the wet FGD scrubber to react with SO_2 in the flue gas and generate calcium sulfite ($CaSO_3$•0.5 H_2O). This unstable by-product is further oxidized by O_2 and stabilized as calcium sulfate ($CaSO_4$•2H_2O). The reaction equations of the wet scrubber are shown below. Lime used as the reagent:

$$[1] \quad CaO_{(s)}(Lime) + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)}$$

$$[2] \quad Ca(OH)_{2(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} + H_2O_{(l)}$$

[3] $2CaSO_{3(s)} + O_{2(g)} + 4H_2O_{(l)} \rightarrow 2(CaSO_{4(s)} \bullet 2H_2O)_{(s)}$ (FGD gypsum)

Limestone used as the reagent:

[4] $SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$

[5] $CaCO_{3(s)}(limestone) + H_2SO_{3(aq)} \rightarrow CaSO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$

[6] $2CaSO_{3(s)} + O_{2(g)} + 4H_2O_{(l)} \rightarrow 2(CaSO_{4(s)} \bullet 2H_2O)_{(s)}$ (FGD gypsum)

Figure 1 shows the process of wet FGD gypsum generation.[3] Figure 2 shows the diagram of a wet FGD scrubber.[4] For a dry FGD scrubber, which is placed before the ESP and baghouse, calcium oxide is used as the reagent, which directly reacts with SO_2 in a fluidized bed and generates the dry by-product ($CaSO_3$). These dry by-products are subsequently collected by the ESP and the baghouse.

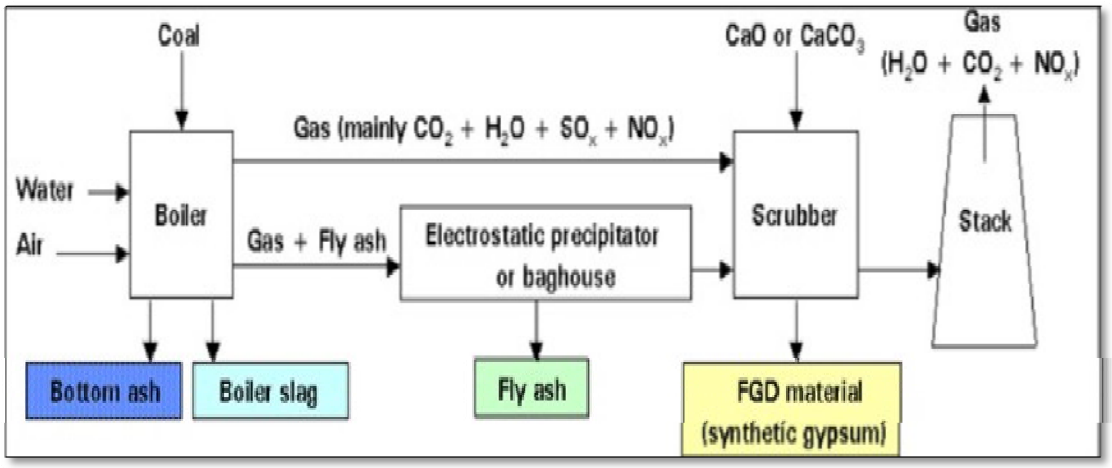


Figure 1. Flow diagram of the FGD process based on lime or limestone.

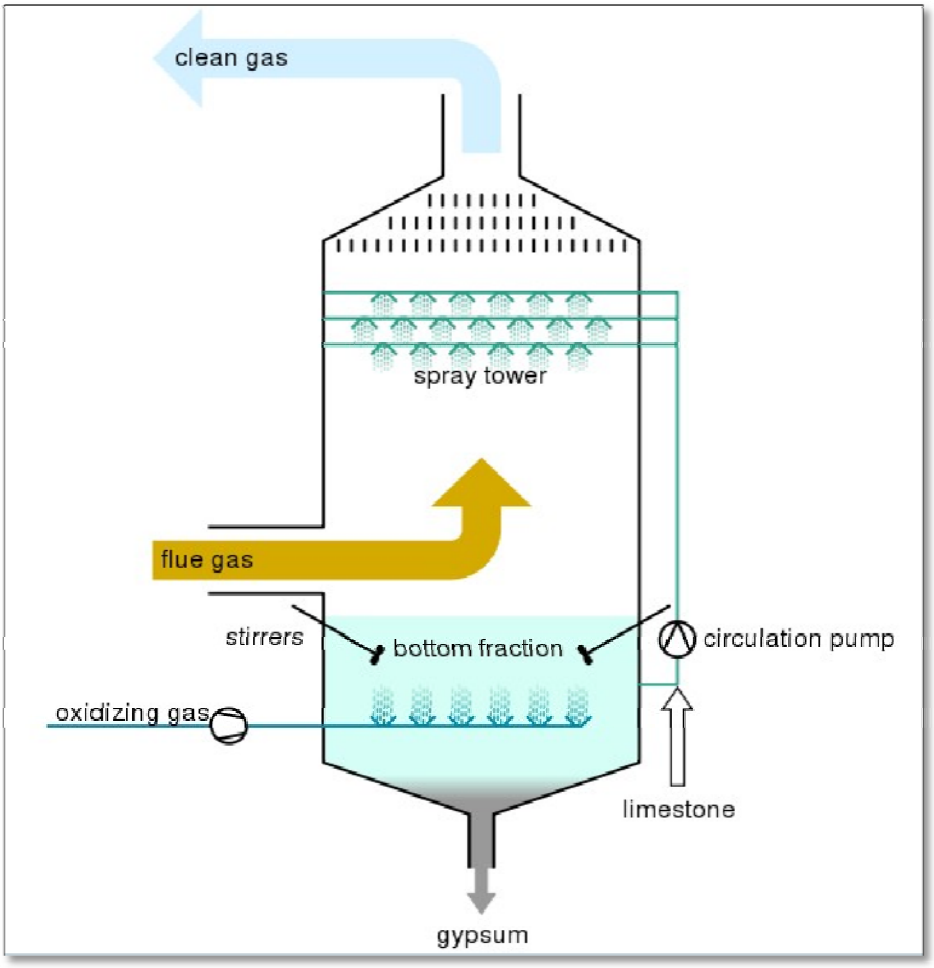


Figure 2. Diagram of flue gas desulfurization scrubber.

1.3 Applications of Flue Gas Desulphurization Gypsum

FGD gypsum consists of small, fine particles, which are widely used in many industrial and agricultural processes. They are used as raw materials for wallboard, fill material for structural applications and embankments, feed stock in the production of cement, raw material in concrete products and grout, and ingredients in waste stabilization and solidification.[5] However, the market for the previously mentioned applications of gypsum is quickly saturated because of the increase in production of gypsum in coal-fired power plants. Therefore the interest in land application of gypsum has been grown. Field studies indicate that FGD gypsum improves soil quality by altering

the chemical and physical characteristics of soil. According to Ritchey and V. C. Baligar's study, FGD gypsum can mitigate soil acidity, supply nutrients and increase phosphorus availability.[6] These results were similar with R. B. Clark et al. studies, who found that FGD gypsum can mitigate soil acidity, provide nutrients to plants (such as magnesium, potassium, zinc, copper and boron), improve soil physical properties and reduce phosphorus availability.[7] FGD gypsum use increases the efficiencies of nitrogen and phosphorous.[8] FGD gypsum can also increase yields according to the results of Dick Wolkowski et al.[9]

1.4 Concerns about FGD Gypsum Amended Soil

While a large amount of research has demonstrated the beneficial use of FGD gypsum on agricultural land, concerns about safety and effectiveness of FGD gypsum amended soil warrants additional study. FGD application may lead to the constraint that excess soluble salts and large amounts of calcium imbalance other nutrients. In addition, soil and plants may be contaminated by toxic trace metals, especially mercury. Mercury may enter the food/water chain and thus lead to serious environmental pollution.

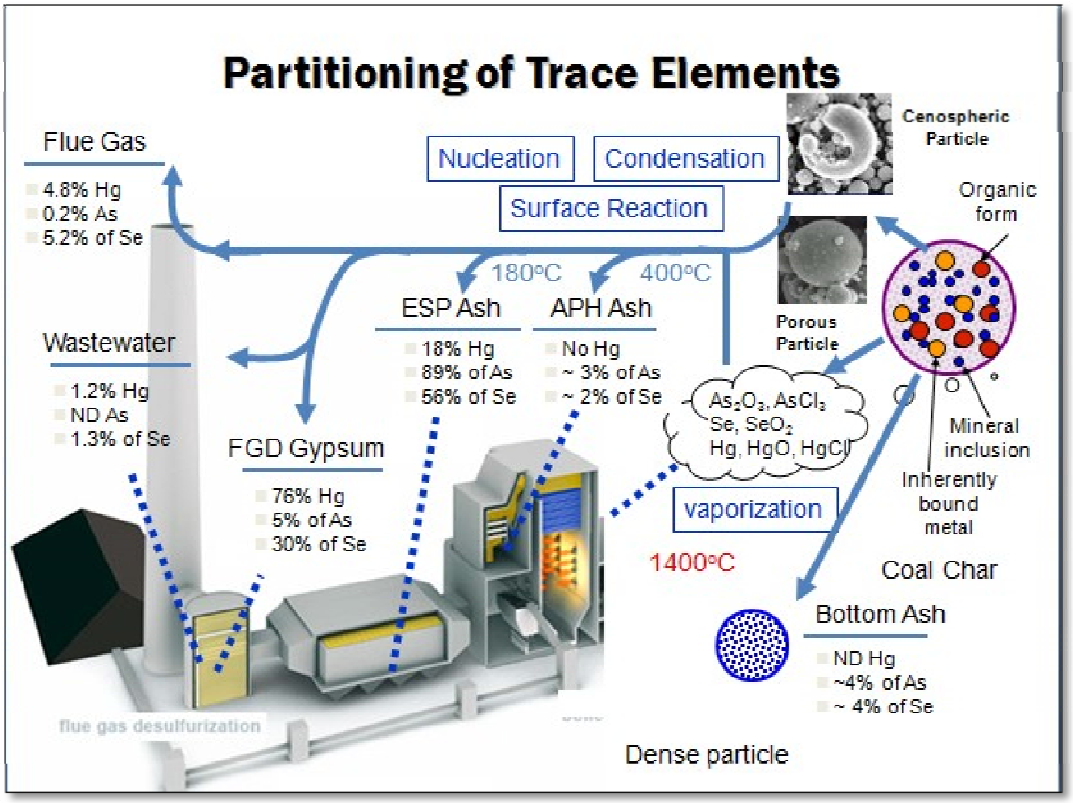


Figure 3. Fate of trace metal of coal in coal fire power plants.

Coal contains small amounts of toxic metals. Some of these metals are captured in FGD gypsum as shown in Figure 3. The U.S. Department of Energy and the Environmental Protection Agency, suggested that the FGD scrubber is helpful for decreasing mercury content in flue gas. Wet FGD technologies can remove highly-soluble oxidized mercury, and if the scrubber is used with SCR, about 85%-90% of the mercury can be captured in wet FGD gypsum.[10-11] Therefore, mercury content in FGD gypsum is of major concern in FGD by-products.

While FGD gypsum improves many characteristics of soil, the concern over toxic metals on human health and environment inhibit its widespread agricultural use. Mercury is more volatile than other elements and can readily evaporate into the atmosphere. It has

been reported that mercury in the soil can emit into the atmosphere and be absorbed by plants.[12]

Most of the mercury in FGD gypsum exists as inorganic mercury sulfide and mercury chloride. These forms of mercury have a lower health threat than elemental and organic mercury. However, bacteria, organic matter and other factors in soil can reduce inorganic mercury into organic and elemental mercury, which can evaporate into the environment, thus, increasing the mercury content in the atmosphere. Furthermore, methyl mercury is easily absorbed by plants and is bio-accumulated by fish or other animals, and thus enters the food-chain. Mercury is hazardous to human health because it accumulates and is difficult to remove from the body. Therefore, it is very important to determine the mercury transport of FGD gypsum treated soil, and its determining factors.

1.5 Similar Research Efforts

Many factors lead to mercury evaporation from soil, such as moisture, soil pH, soil composition, solar radiation, mercury concentration and mercury speciation.

First of all, not all mercury species in the soil can evaporate into the environment. Only elemental mercury and dimethyl mercury are considered volatile. Enzymes can convert the inorganic mercury to "volatile" mercury. Organic matter and bacteria have been reported to be predominant factors which affect mercury evaporation rate. For example, Fe (III)-reducing bacteria can help inorganic mercury convert into dimethyl mercury according to the experimental results of Lisamarie Windham-Myers et al.[13] In addition, humic acid, fulvic acid and dissolved organic matter can convert inorganic mercury into dimethyl mercury.[14] Furthermore, with increasing pH, the effect of DOM

(Dissolved Organic Matter) on mercury (II) reduction becomes stronger.[15] Carbon, sulfur and iron cooperate with sulphate-reducing bacteria to enhance mercury methylation.[16]

Additionally, soil moisture enhances mercury evaporation.[17] In Xiaoxi Song's single and multiple rainfall experiments, the results of a single heavy rainfall, just one time, can lead to an increase in mercury emission. In multiple rainfall experiments, only the first rain leads to an increase in mercury emission, whereas the following two rainfalls did not produce the expected additional emission. It was concluded that rainfall can contribute to mercury emission in dry soil, but the effect decreases when soil moisture is increased.[18]

Mercury emission from soil is also related to soil temperature and solar radiation.[19] Bare and plant covered soil should be considered separately. In bare soil, mercury concentration and soil temperature determine mercury transport in the soil. In the soil supporting plants, mercury transport is more responsive to solar radiation.[20]

Mercury in the soil also can be uptaked by plants. The process of mercury absorption by plants can be divided into two parts: adsorption and transportation. These two processes have been reported to be independent of each other. Different plant species have different mercury absorption rates and mass limitations.[21, 22] In addition, the mercury uptake rates are independent of mercury concentration in the soil. When it comes to mercury distribution in plants, the mercury concentration in the stem is much lower than in leaves and roots, which is shown in Figure 4[23] and Table 1.[23]According to the study of Jose Antonio Molina et al., the mercury in the roots and leaves is around 30 ng/g, and the mercury in the stem is around 5 ng/g. This indicates that mercury transportation within the plant is limited. The mercury in the leaves results from absorption from the atmosphere. When a plant defoliates, the leaves fall down, and

mercury enters the soil and is absorbed by the plant's roots. Mercury in the plant's roots stays in the plant's roots.

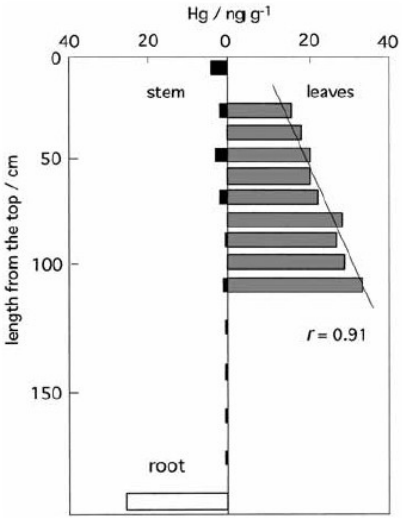


Figure 4. Distribution of mercury in plants.

Table 1. Effect of added mercury to soil on the mercury distribution in the plant body.

Plant parts	Mercury contents (ng/g[a])	
	Background (n=19)	Mercury addition[b] (n=2)
Leaves[c]	17.9±7.7	18.3±6.1
Stems[c]	2.8±2.4	5.6±1.5
Roots	53±98	2000±307
Soil	160±178	497

a. Wet weight basis

b. 200ml of 1 mg/L $HgCl_2$ solution (as mercury) was added into the soil every two days (total 4 times)

c. Mean concentration of each sample plant

Almost all the previous research and conclusions were made without reporting the source of mercury. In this study, FGD gypsum was the predominant source of mercury.

FGD gypsum is not the source of background mercury in the soil, but it does affect mercury transport in soil due to changing soil characteristics.

2. Experimental

The project was carried out in two phases: greenhouse and field study. The greenhouse study was divided into three parts: (1) Tall fescue; (2) Moisture study; and (3) Cherry radish/Lamium amplexicaule. The greenhouse studies were carried out periodically during March 2011- February 2012. The field study was carried out on May 2011- September 2011.

2.1 Material

The project utilized two types of soil. One came from Heritage farms with a mercury concentration of 20 – 25 ppb. The other soil came from Wal-Mart (organic soil) and its mercury concentration was 32 ppb (organic soil).

FGD gypsum came from a regional coal-fired power plant and its mercury concentration was 300 ppb.

Mined gypsum came from a local lawn and garden center and its mercury concentration was 300 ppb.

Type II de-ionized water (15 MΩ) was used for the irrigation water. The mercury concentration was below the detection limit.

Four different plants species were used in this study. Corn was used in field study. Tall fescue, cherry radish and lamium amplexicaule (L.A.) were used in the greenhouse. Tall fescue is the most common grass in Kentucky. L.A. is a grass, naturally grown from the soil. When the plants ripen, the seeds of Tall fescue and L.A. were on the top of the plants, whereas the cherry radish was under the soil. Thus, cherry radish has a different nutrient trend compared to tall fescue and lamium amplexicaule.

2.2 Sample Handing and Preservation

Four different matrix samples are presented in the greenhouse and field study: soil, plants, activated carbon and infiltration water.

Soils were sampled by probe for a specified time and separated into different layers. The soils belonging to the same layer and the same chamber were mixed and ground together prior to analysis. Figure 5 shows the image of the probe. Samples were air dried at 40ºC for 72 hours in order to reduce moisture content and then crushed prior to analysis.

Corn plants were sampled at the end of the season and allowed to air dry in a dark dry room. After two months, the dry corn was weighed and then crushed prior to analysis.

Plants (tall fescue, cherry radish and lamium amplexicaule) were pulled out gently from the soil taking care not to break the roots, air-dried at 40ºC for 72 hours and washed with de-ionized water. After that, they were separated into different parts: leaves, stems, and roots, and washed with de-ionized water again. Finally, they were air dried at 40ºC again for 72 hours and then crushed prior to analysis.

The infiltration water was collected at the bottom of the greenhouse and put into 125ml polypropylene screw bottles.

The mercury in air was collected using activated carbon traps. In the greenhouse study, the activated carbon traps were collected at the end of the experimental period (33 days). In the field study, the activated carbon traps were collected during June and July. Collection times for the field studies were 10 days.

Figure 5. Image of probe.

2.3 Analytical Methods

Mercury Analysis

Many instruments and methods are available for analyzing the content of mercury in liquid and solid samples. Atomic Fluorescence Spectrometry (AFS), Atomic Absorption Spectrometry (AAS), and Inductive Coupled Plasma (ICP) are principally applied for inorganic element analysis.

In these studies, plants, soil, infiltration water, and activated carbon traps were analyzed by LECO AMA 254, Leeman Hydra C and Ohio Lumex, which are based on cold-vapor atomic absorbance spectrometry (AAS) techniques. They were designed according to EPA Method 7473. Due to the low boiling point of mercury, most mercury digestion processes lead to mercury loss. Thus eliminating digestion is an efficient way to improve mercury recovery. Mercury content of the samples is normally at the part per

billion level. A check standard was performed for every 10 runs to measure the accuracy of the data.

Soil Quality Analysis

pH test: Orion star series meter (5 star degrees) was employed to analyze pH values. Before analyzing, the pH meter was calibrated with Orion 4.0, 7.0, and 10.0 buffer solutions.

Carbon, hydrogen, and nitrogen: The soil samples were tested using a LECO TruSpec CHN analyzer to determine carbon, nitrogen, and hydrogen content.

2.4 Instrumentation

Leeman Hydra C

Figure 6[24]shows the image of Leeman Hydra C. Hydra C is a mercury analyzer based on the US EPA method 7473. The samples were dried at 300℃ and then burned at 800℃ in a stream of oxygen. After combustion, the gases pass through a catalyst tube to remove halogens, nitrogen oxides, and sulfur oxides. The gases then pass through the gold tube (amalgamation tube) which captures the mercury vapor. The gold tube was subsequently heated to 600℃ to release the mercury which was detected by a cold vapor atomic absorption spectrometer (CVAAS). There are two sensitivity cells (a high sensitivity cell and a low sensitivity cell) in the hydra C. These two cells provide a wide dynamic range of linearity. The analysis is completed by measuring the absorbance at 253.7nm. Figure 7 shows an example of absorbance spectrum.

Figure 6. Hydra C.

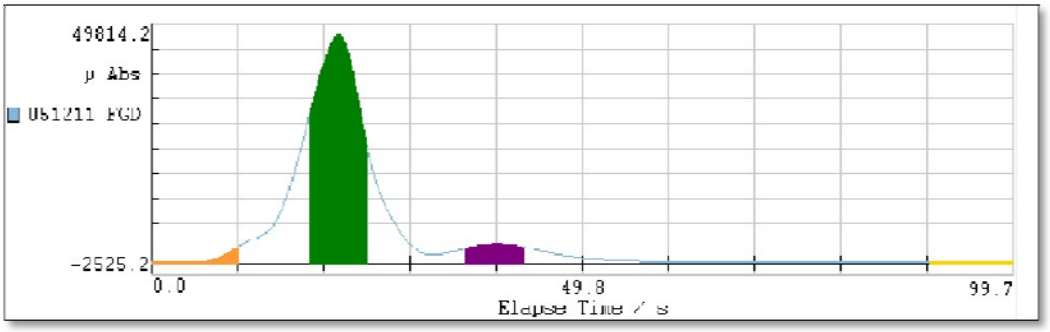


Figure 7. Spectrum of example sample.

Different instrumental conditions were applied in order to get good results for the matrix sample. The different conditions are listed in Table 2.[25]

Table 2. Leeman Hydra C analysis conditions.

Parameter \ Type	Infiltration water	Soil	Plants	FGD gypsum
Drying temperature(ºC)	300	300	300	300
Drying time (s)	35	10	35	60
Decomposition temperature (ºC)	800	850	800	800
Decomposition time (s)	120	180	160	400
Catalyst temperature (ºC)	600	600	600	600
Wait time (s)	60	60	60	60
Amalgamator temperature (ºC)	600	600	600	600
Amalgamator Time (s)	30	30	30	30

LECO AMA 254

The mechanism of LECO AMA 254 is similar to a Hydra C mercury analyzer. An image of AMA 254 is shown in Figure 8.[26] The first stage of an analysis is known as the decomposition phase. Solid or liquid samples are converted into the gaseous phase in the combustion tube, which provides the energy, around 750℃. After that, the gaseous material is allowed to pass into the catalyst portion, which absorbs the SO_2, NO_x, and halogens in order to produce a clean gas. The amalgamator tube has a high chemical affinity to mercury, so the amalgamator tube is employed to absorb mercury from the cleaned gas and subsequently release them into the detector upon heating, typically around 900℃. A standard Atomic Absorption Spectrometry and a silicon UV diode detector are applied for mercury quantization.

LECO AMA 254 is very similar to the Hydra C, which can analyze many different samples, such as coal, coke, water, soil and fish. In this study, AMA 254 was generally used to analyze FGD gypsum, soil, infiltration water and plants.

Figure 8. Image of AMA 254 mercury analyzer.

LECO TruSpec CHN

LECO TruSpec CHN was employed to determine the content of carbon, hydrogen and nitrogen in the soil. It was designed according to ASTM (American Society for Testing and Material) Method D 5373-08 and Method 4239-08. Carbon, hydrogen and nitrogen were determined in a single instrumental procedure. Helium was employed as carrier gas, and oxygen was employed as combustion gas. Under high temperatures, the sample was burned in high purity oxygen. After combustion, carbon and hydrogen were converted into their corresponding gases (CO_2 and H_2O). All interference gases were removed before the mixture gas enter detector. The carbon dioxide and water vapor in the gas stream was determined by detector. The NO_x is reduced to N_2 using a copper catalysis before quantification using a Thermal Conductivity Detector (TCD).

Ohio Lumex RA 915^+

Ohio Lumex RA 915^{+} was used for the activated carbon analysis, which was attached with a PR-91C pyrolysis attachment. The PR-91C pyrolysis attachment was employed to enhance the capabilities of the RA 915^{+} for our particular matrix sample. Ohio Lumex is based on Zeeman Atomic Absorption Spectrometry, which use High Frequency Modulation of Light Polarization ZAAS-HFM.[27] In the analysis procedure, the mercury in the sample is converted from a bound state to atomic state through thermal decomposition in a two section atomizer. The majority of the mercury compounds were decomposed in the first section and the remaining mercury compounds were completely decomposed after the second section, in which the temperature is 800℃. All organic and carbon particles were converted to carbon dioxide and water after combustion. The detection limit for activated carbon is 0.5 μg/Kg.

2.5 Greenhouse

The greenhouses were made from 6 mm acrylic plastic. Each greenhouse includes three chambers. Each chamber was 30.5 cm^2 and approximate 76cm tall, as shown in Figure 9. Drainage valves were placed in the bottom of each chamber, as well as, two holes, approx middle height, for sampling air in and out. Permeable plastic material was placed in the bottom of each chamber to hold the soil in place, but also allow for drainage of moisture. Sunlight systems were located on the top of each greenhouse. The sunlight system came from Sunlight Supply, Inc. Two different models of sunlight were used, SS-7 MH 400 and SS-7 HPS 600. The irrigation systems were installed at the top of each section of the greenhouse chamber. Air sampling pumps were used to control the airflow rate.

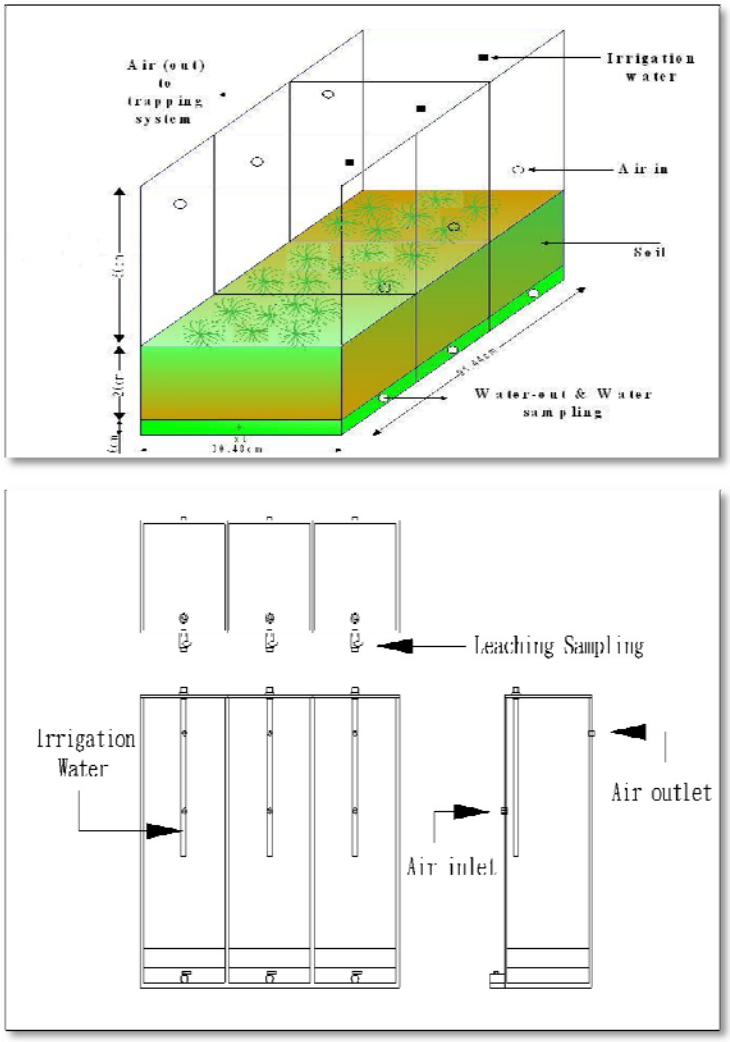


Figure 9. Schematic description of greenhouse chamber.

2.6 Greenhouse Study

2.6.1 Tall Fescue Study

The first study was carried out in March 2011. The objective was to determine the effect of different amounts of FGD gypsum on mercury transport. Two greenhouses were used, six chambers total. Important parameters are listed in Table 3.

Table 3. Tall fescue parameters.

Parameter	Sample
Soil	Heritage farms 25 ppb mercury
Plant	Tall fescue, seed with 65 ppb mercury
Sunlight system	Five hours/day
Fertilizer	Chicken waste 17 ppb mercury
Growth period	March 2011-April 2011, 6 weeks in total
Analytical technique	Leeman Hydra C

Figure 10 displays the layering of a chamber. In the bottom of the chamber, we placed permeable plastic material, followed by 15 kg of soil. Then we added 1 kg soil, varying amounts of FGD gypsum, 0.1 kg chicken waste and 5 g tall fescue seeds were mixed evenly. The chicken waste was a source for plant nutrients. At the beginning, the soil was completely dry, and thus around 3 L of water was added to moisten the soil for proper crop growth.

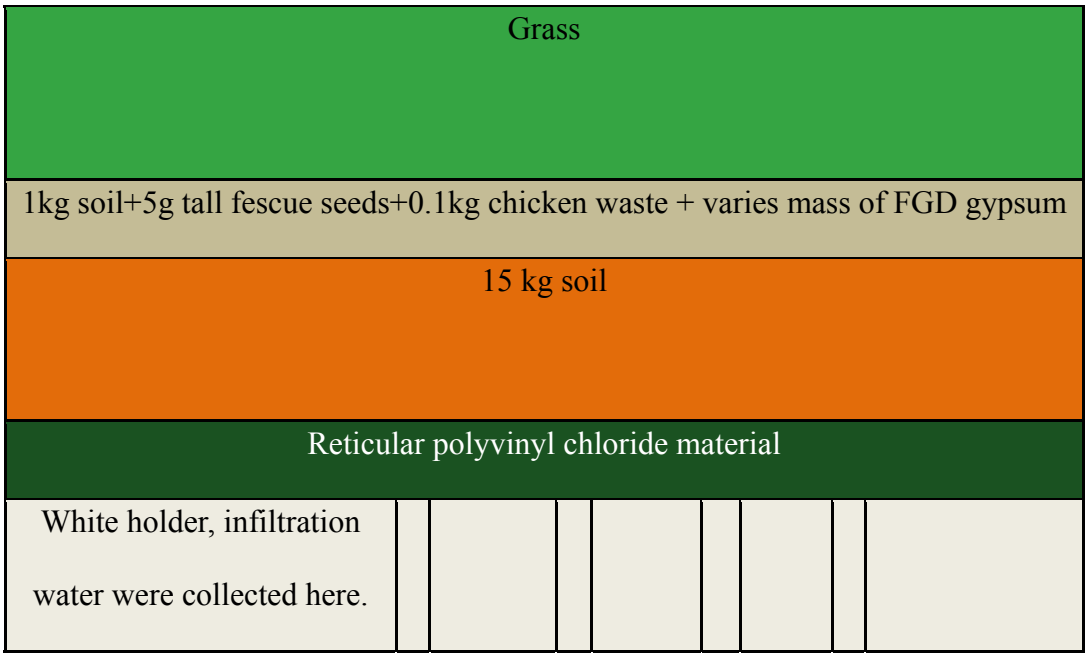


Figure 10. Diagram of material in each chamber.

In this stage, different amounts of FGD gypsum were added into each chamber, the variation was provided in Table 4. These conditions were duplicated in the second greenhouse.

Table 4. Variations of tall fescue study.

Chamber	Chamber1 (Control)	Chamber 2	Chamber 3
FGD gypsum	No gypsum	0.5 kg	1 kg

The soil samples were collected after watering (Initial soil) and at the end of this study (Final soil). And for a given chamber, the soil was sampled in three locations. Soil was separated into four parts by mass and labeled as layer 1 (top), layer 2, layer 3, and layer 4 (bottom). All soil samples from this study were analyzed by Leeman Hydra C.

Tall fescue was sampled at the end of this study. All tall fescue was pulled out gently from the soil in order to get the root. After drying, the tall fescue was weighed prior to mercury concentration determination. At the end of this study, infiltration water

was collected from the valve of the greenhouse bottom. 50 µl of infiltration water was loaded into hydra C sampling boats and analyzed.

2.6.2 Moisture Study

The moisture study was carried out in August 2011. In a previous study carried out by Chin-Min Cheng and Yuang-Nan Chang, in which the effect of water on mercury evaporation from FGD gypsum amended soil, was studied. They concluded that mercury emission is affected by the ratio of FGD gypsum in the soil and soil moisture[28]. In order to further investigate the effect of mercury transport in FGD gypsum amended soil, moisture studies were carried out in two batches to study the effect of a single heavy rainfall (batch one) and multiple different rainfalls (batch two). Four greenhouses were employed, twelve chambers total. The important parameters are listed in Table 5.

Table 5. Important parameters in moisture study.

Parameter	Sample
Soil	Batch 1: Heritage Farms, Clay soil (25 ppb mercury) Batch 2: Earthgro, Organic soil (32 ppb mercury)
Plant	N.A.
Sunlight	Natural sunlight. 8:00am-4:00pm
Analytical technique	LECO AMA 254

In batch one, 1 kg soil, different amounts of FGD gypsum, and 0.1 kg chicken waste were mixed evenly. This mixture was applied after adding 15 kg of soil. Figure 11 indicates a diagram of a given chamber of these two greenhouses. Water application was 40 inches/year.

$$\frac{40inch}{365day} \times 2.54 \frac{cm}{inch} \times 30.48cm \times 30.48cm = 258.6mL$$

Therefore, 260 ml de-ionized water was applied to Batch 1 every day.

In Batch 2, all the chambers were applied 0.05 kg FGD gypsum and chicken waste. The only variation in Batch 2 is the rainfall for every chamber. The variation is shown in Table 6 and Table 7. In addition, the soil samples are different in these two batches, and thus the effect of different soil on mercury transport from FGD gypsum amended soil is also measured. Water application was 20 inches/year, 40 inches/year and 80 inches/ year, respectively. Therefore, 130 ml, 260 ml and 520 ml de-ionized water were applied to each chamber every day.

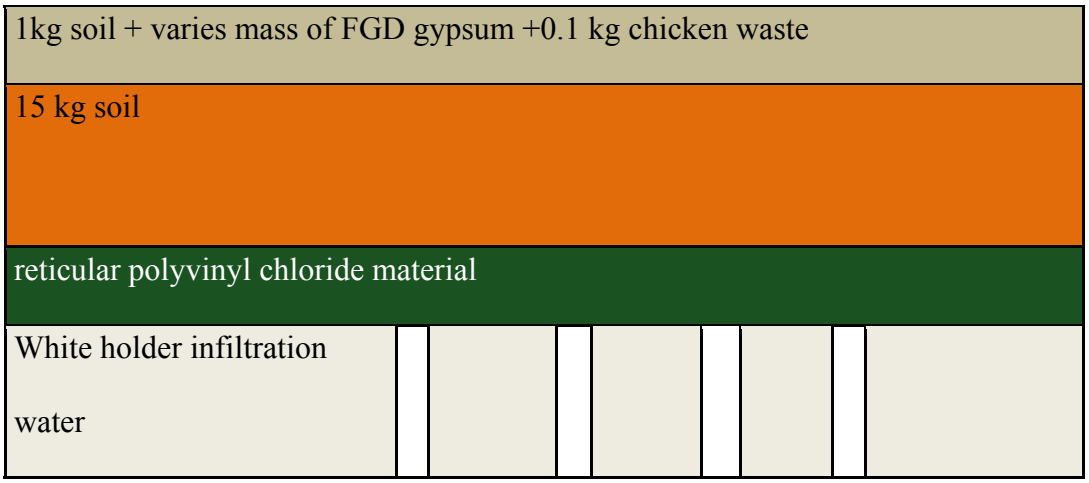


Figure 11. Different material in each chamber.

Table 6. Variation of moisture study: Batch 1.

	Chamber 1	Chamber 2	Chamber 3
FGD gypsum	No gypsum	0.05 kg	0.1 kg
DI water	260 ml every day	260 ml every day	260 ml every day
Soil	Clay type	Clay type	Clay type

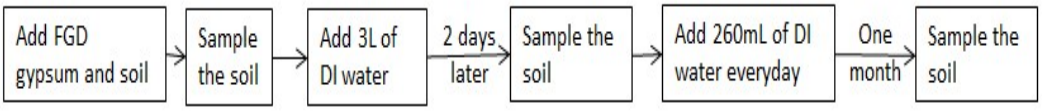
Table 7. Variation of moisture study: Batch 2.

Chamber	Chamber 1	Chamber 2	Chamber 3
FGD gypsum	0.05 kg	0.05 kg	0.05 kg
DI water	130 ml every day	260 ml every day	520 ml every day
Soil	Organic type	Organic type	Organic type

In Batch 1, soil samples were collected and labeled as layers 1 and 2 when adding the soil and gypsum into the chamber. At this time, all the soils are completely dry. 3L of de-ionized water was then added into each chamber to moisten the soil. After water went through all soil layers, the soils were sampled again. The moistening process took two days. Soil samples were collected again at the end of this study (30 days).

In Batch 2, 3 L of de-ionized water was used to moisten the soil. The soil samples were collected and labeled as layer 1 and layer 2 after watering and at the end of this study. The procedures are shown as Figure 12.

Batch 1



Batch 2

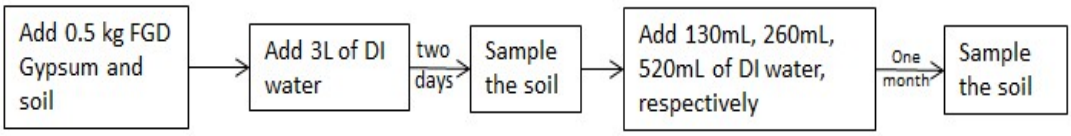


Figure 12. Moisture study procedure.

2.6.3 Cherry Radish/ Lamium Amplexicaule Study

This study was carried out on February 2012. This study was conducted to understand the effect of different plants on mercury transport in FGD treated soil. Two greenhouses were used, six chambers total. Important parameters are listed in Table 8.

Table 8. Important parameters for cherry radish study.

Parameter	Sample
Soil	21 ppb mercury
Plant	Cherry radish, Lamium amplexicaule (L.A.)
Sunlight system	Twelve hours/day
Growth period	January 30th-March 1st
Analytical technique	Mercury analysis: LECO AMA 254; Ohio Lumex
	Soil quality analysis: LECO CHN; TGA; Orion star series meter (pH meter)

Initially 10 kg of dry soil (21 ppb) was added to each chamber (12 cm deep). 350 mL of de-ionized water was added to each chamber to moisten the dry soil in order to

promote plant growth. After that, different amounts of FGD gypsum were added to each chamber and mixed with surface soil. The variation is shown in Table 9.

Table 9. Variations FGD gypsum application.

Chamber	FGD gypsum (kg)
1 (Control)	None
2	0.01
3	0.05
4	0.1
5	0.5
6	1

Soil was then sampled and air-dried for 72 hours. After collecting the soil samples, ten seeds were planted in a row. The radish seeds were planted 2cm deep and exposed to artificial sunlight approximately 12 hours each day. Chambers were watered on an "as needed" basis, with a total amount of 2,300 ml of de-ionized water.

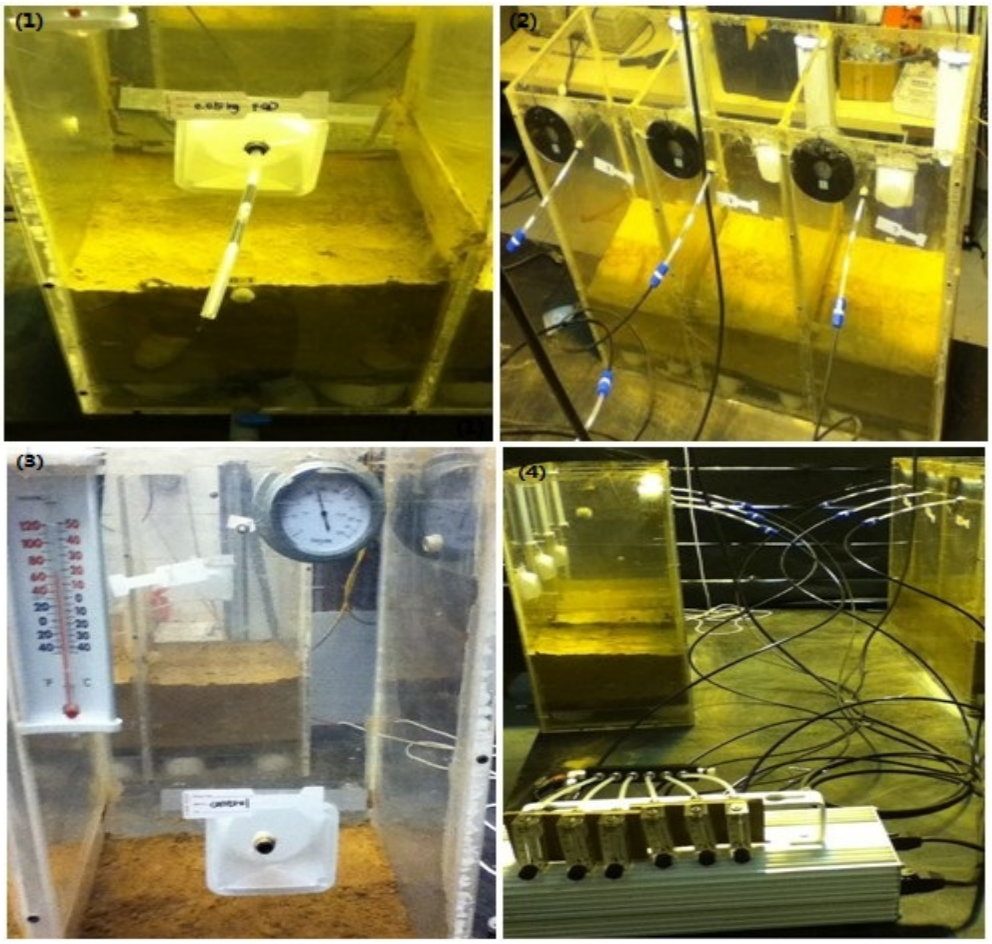


Figure 13. Installation view. (1) Air in activated carbon trap (2) Air out activated carbon trap (3) Thermometer and hygrometer (4) Full view.

Figure 13 shows the experimental setup for measuring the emission of mercury into the atmosphere. Activated carbon traps have a strong affinity for absorbing elemental mercury. Therefore, we connected our carbon traps in-line with a flow meter, which is also connected with a vacuum pump to draw the air out of the greenhouse chamber. The flow rate was 0.3 m^3/hour, and thus the air retention time in the greenhouse chamber was about 12 minutes. For a given chamber, one carbon trap was placed at the inlet port, located at the center (43cm from the bottom and 15.2 cm away from two edges) in order to provide mercury free air. Another sorbent trap was placed at the outlet port, where it

was 15.2 cm away from each side of the edge and 65 cm above the bottom of the greenhouse chamber, which acted as our absorbing medium. The carbon traps consisted of a 10-mm diameter glass tube, about 12 cm in length filled with granules of halogenated carbon. Three 1cm segments of glass wool filled at the tip, middle, and the end of the sorbent trap, which divided the halogenated carbon into two sections. The first section was used to capture mercury and the second section was used to check that no mercury escaped the first section. Each activated carbon trap had 0.14 g halogenated carbon added to each section of air-out side, whereas the carbon trap located in air-in side was only one section with really loose glass wool. The loose glass wool minimized the air restriction on entering the chamber and thus a large negative pressure in the chamber was avoided. A layer of reticular polyvinyl chloride material was placed at the bottom of the soil section so that the infiltrated water could be collected from the bottom valve of each chamber.

Mercury Analysis

The soil samples were separated by mass into three parts after drying completely and labeled as Layer 1, Layer 2 and Layer 3. Soil samples also were collected from the roots of the lamium amplexicaule and cherry radish plants. These soil samples were labeled as the soil adjacent to roots.

After collecting the soil from the lamium amplexicaule and cherry radish, the plants were rinsed with de-ionized water. Lamium amplexicaule were separate into roots, stems and leaves. Cherry radishes were separated into roots and stems/leaves.

In this study, the soil qualities (pH, carbon, hydrogen, and nitrogen) were analyzed.

The soils were sampled both before and after applying FGD gypsum for pH. Approximately 5 grams of soil from different soil sample was loaded into 50-ml tubes. Five milliliter of de-ionized water was mixed with the soil. The samples were stirred vigorously for 5 seconds. After standing for 10 minutes, the electrode was placed into the slurry.

The carbon, hydrogen, and nitrogen instrument is highly automated. Samples are weighed and then placed inside the instrument, which operates automatically. QC/QA samples were performed for every 10 runs.

2.7 Field Study

Fieldwork was started on May 12th, 2011 and finished on September 14th, 2011. The location of the fieldwork was Heritage Farms, 4285 Sugar Grove RD, Bowling Green, KY. Typical rainfall for this location is 40 inch/year.

This study consisted of 9 plots. There were three control plots, three mined gypsum plots (natural gypsum plots), and three FGD gypsum plots. Each plot is 20 feet by 30 feet. Except the end plots (Control 1 and FGD gypsum 3) were twice as wide. A 10 foot buffer space separated the plots. Figure 14 displays the field study. On May 12, 2011, three mined gypsum plots were treated with natural gypsum at rate of 5000 lb/acre, and three FGD gypsum plots were treated with FGD gypsum at rate of 5000 lb/acre. The FGD gypsum came from a regional power plant. Corn was employed as plant sample. The growth period was 4 months, from May 2011-August 2011.

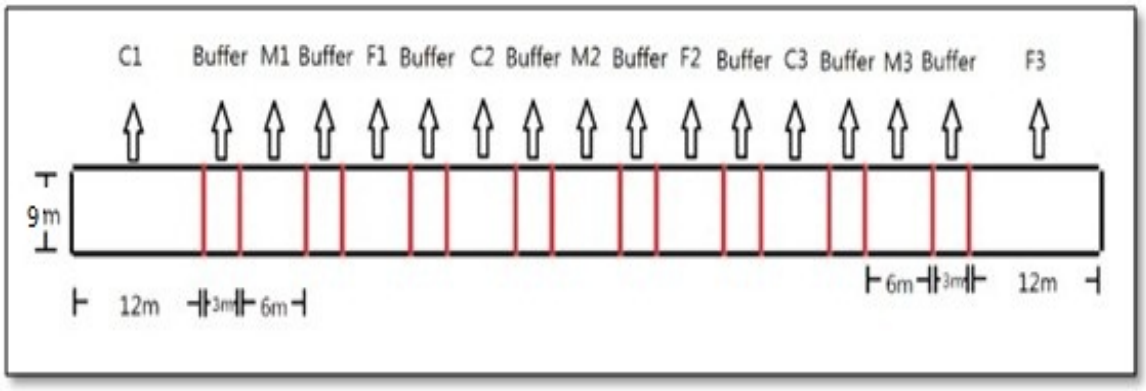


Figure 14. Field study. C1 refers to Control 1, M 1 refers to Mined 1 and F1 refers to FGD 1. C1 and F3 are 12 meters by 9 meters; other plots are 6 meters by 9 meters.

The corn seeds were planted on May 28 2011. All the seeds were germinated after approximately 15 days, the corn plants are shown in Figure 15.

Figure 15. Corn seeding.

In the field study, the same activated carbon traps as with the greenhouse study were used to capture the mercury in the air. For a given plant, six activated carbon traps were installed in order to analyze the mercury emission from different heights. Figure 16 displays carbon traps location. Air was sampled from June 1st and turned off on June 11th and from August 1th to August 11th. For the Control 1 and FGD 3 plots, six activated carbon traps were installed at different heights in order to develop a concentration

gradient of mercury above the ground. The traps were placed so that ambient air would be drawn in from a vacuum pump with a flow meter (10 ft^3/hour) connected in-line. The air was sampled for 10 days.

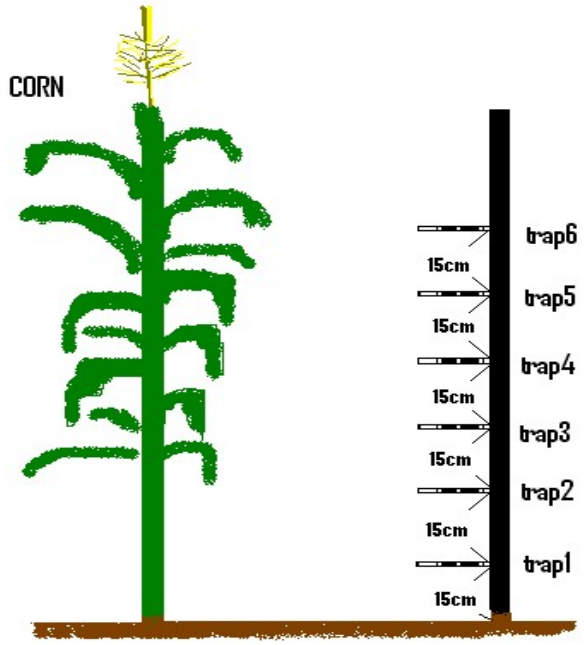


Figure 16. Location of activated carbon traps.

On September 14th, the corn was sampled. For each plot, five whole stalks (corn cob, root, stem and leaves) and three rows of corn cobs were collected. After drying all the samples, five whole stalks were crushed to a powder. Kernels were also collected from the corn cobs and crushed to a powder.

3. Results and Discussion

3.1 Tall Fescue Study

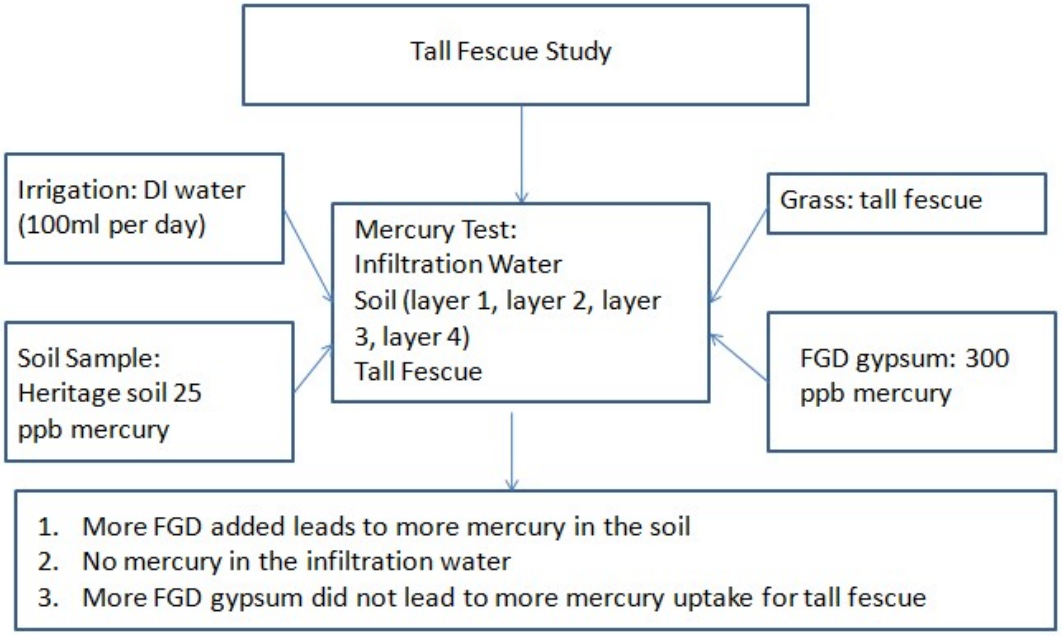


Figure 17. Flow chart of tall fescue study.

3.1.1 Mercury Concentration in Soil

Mercury concentration in soil for different depths is listed in Table 10.

Table 10. Mercury concentration (ppb) for different depths.

ID	Week 1	Week 6
Control Layer 1	23±1	21±0
Control Layer 2	25±1	23±0
Control Layer 3	27±2	27±1
Control Layer 4	30±1	26±2
0.5kg FGD gypsum Layer 1	64±0	59±1
0.5kg FGD gypsum Layer 2	38±0	27±2
0.5kg FGD gypsum Layer 3	27±2	26±1
0.5kg FGD gypsum Layer 4	28±1	27±0
1 kg FGD gypsum Layer 1	102±1	84±2
1 kg FGD gypsum Layer 2	40±2	31±1
1 kg FGD gypsum Layer 3	20±0	28±0
1 kg FGD gypsum Layer 4	29±0	27±1

Since FGD gypsum was applied to the surface of the soil, the mercury concentration on top was initially higher than the deeper soils. In the application of 0.5 kg gypsum per chamber, the mercury concentration of layer 1 increased by 156%, and in the 1 kg chamber, it increased by 300%. The mercury concentration in layer 2 for both 0.5 and 1.0 kg were higher than those in layers 3 and 4 by about 30%. The concentration increase may be caused by water. It has been reported that FGD gypsum has good mobility in the soil, and water is able to accelerate the mobility of FGD gypsum in the soil. At the

beginning, 3 L of water was added to moisten the soil. Due to water infiltration in the subsoil, FGD gypsum arrived at layer 2 and thus leads to a mercury concentration increase. Soil structure may impact mercury transport and penetration into the soil. The compacted soil likely inhibits FGD gypsum penetration into layers 3 and 4. Overall, soil compaction and gypsum application methods impacted the mercury concentration at different soil depths.

For every chamber, the mercury concentration of layers 1 and 2 decreased after six weeks, but there was no mercury increase in layers 3 and 4. This may indicate that the reduction of mercury concentration in layers 1 and 2 resulted from tall fescue uptake and mercury emission. The mercury did not penetrate layers 3 and 4 during the whole experimental period.

3.1.2 Mercury in the Tall Fescue

Table 11 gives the yield of tall fescue harvested and the mercury concentration. The 0.5 kg rate produced a greater amount of tall fescue than the 1 kg rate. Tall fescue uptakes more mercury from the soil in the 0.5 kg chamber than in the 1 kg chamber.

Table 11. Mercury concentration and harvest mass.

Parameter / FGD gypsum mass	Tall fescue mass (g)	Mercury concentration (ppb)
1 kg	98	56±3
0.5 kg	153	76±3
Control (No FGD)	168	51±1

In this study, tall fescue mass decreased significantly after FGD gypsum application. In normal conditions, FGD gypsum is applied to soils typically at 5000 pounds/acre. In

the greenhouse study, 0.01 kg FGD gypsum should have been added into every chamber based on the field study. Therefore, the over dosage of FGD gypsum resulted in a negative effect on growth of tall fescue.

Furthermore, the tall fescue study shows the highest mercury concentration in 0.5 kg gypsum chamber, which is higher than those in 1 kg and control chambers by about 38%. In addition, the mercury concentration of tall fescue in the 1 kg gypsum chamber is relatively similar to that in the control chamber, which indicates that more FGD gypsum did not lead to increased mercury uptake. This could be an indicator that the ability of tall fescue to absorb mercury was limited and that mercury could also poison the roots, leading to low yield and low mercury uptake.

3.1.3 Mercury in Infiltration Water

Mercury concentration in infiltration water was listed in Table 12.

Table 12. Mercury concentration in infiltration water.

Chamber	Mercury concentration (ppb)
1 kg FGD gypsum	2±2
0.5 kg FGD gypsum	4±1
Control	4±1

Only minimal mercury was found in the infiltration water, which is in good agreement with the mercury concentration for soils at similar depths. According to the soil mercury data, there is no obvious mercury concentration increase in layers 3 and 4, thus, mercury was not leached from the soil. Because of the good mobility of FGD gypsum, it could be inferred that mercury penetrated into the subsoil and finally leached out of the soil.

3.1.4 Mass Balance Calculation

The mercury concentration in FGD gypsum is 300 ppb. The initial mercury concentration in the soil is 28 ppb. Mercury in seed is 65 ppb. The mercury concentration of de-ionized water is below the detection limit.

Therefore, at initial conditions:

The mass of mercury in the soil:

$$16 \text{ kg} \times 28 \times 10^{-9} = 448{,}000 \text{ ng}$$

Mercury mass in the seeds:

$$5 \text{ g} \times 65 \times 10^{-9} = 325 \text{ ng}$$

Mercury mass in chicken waste:

$$0.1 \text{ kg} \times 17 \times 10^{-9} = 1{,}700 \text{ ng}$$

Table 13 shows the parameters in initial condition.

Table 13. Initial mercury mass (ng).

I.D	Seeds	Soil	FGD gypsum	Chicken waste	DI water[1]	Total
Control	325	448000	N/A	1700	N.D.	450025
0.5kg	325	448000	150000	1700	N.D.	600025
1 kg	325	448000	300000	1700	N.D.	750025

Final conditions (after six weeks of plant growth):

Mercury mass in soil is calculated by equation [7]:

$$[7] \quad \text{Mercury Mass} = M_{soil} \times \sum_{i=0}^{4} C_{soil}$$

Where M_{soil} is the soil mass at each depth, and C_{soil} is the mercury concentration at the respective depths.

For the 1 kg FGD gypsum application rate, the mass of mercury in soil:

$$4\ \text{kg} \times (84 + 31 + 28 + 27) \times 10^{-9} = 680{,}000\ \text{ng}$$

Mercury mass in grass is calculated by the equation [8]:

$$[8] \quad \text{Mercury Mass} = M_{grass} \times C_{grass}$$

Where M_{grass} is the tall fescue mass in each chamber, and C_{grass} is the mercury concentration for the respective tall fescue.

For the 1 kg FGD gypsum application rate, the mass of mercury in the grass:

$$98\ \text{g} \times 56 \times 10^{-9} = 5{,}488\ \text{ng}$$

The total mercury mass balance was shown in table 14.

Table 14. Final mercury mass (ng).

Chamber	Grass	Soil Mixture	Infiltration Water	Total
Control	5488	388000	N.D	393488
0.5kg	11628	556000	N.D	567628
1 kg	8517	680000	N.D	688517

Table 15 shows the recovery for different chambers.

Table 15. Recovery (%) of different chambers.

Chamber	Mercury recovery
Control	91.8
0.5 kg FGD	94.6
1 kg FGD	84.7

In this study, mercury uptake, mercury infiltration and mercury in the soil were considered, but mercury emission was not measured. The recovery is not 100%, which may be due to mercury emission. For the 1 kg FGD gypsum chamber, more mercury

evaporated into the atmosphere, so the 1 kg FGD gypsum chamber has the lowest recovery.

3.2 Moisture Study

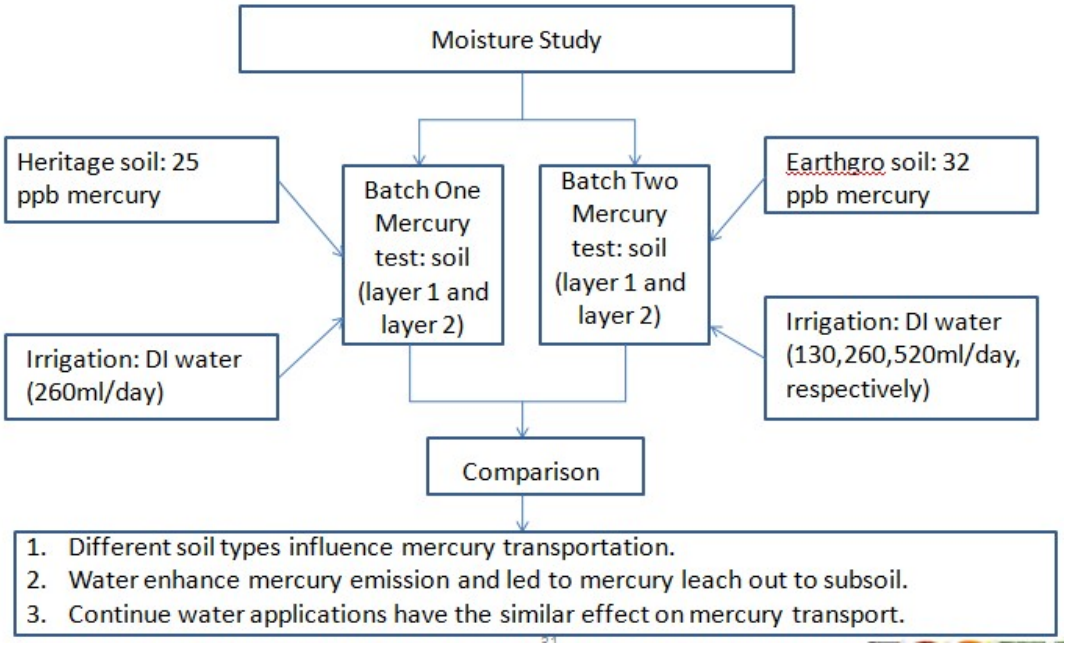


Figure 18. Flow chart of moisture study.

The second study was carried out to investigate the impact of irrigation on mercury transportation.

3.2.1 Effect of a Single Large Rainfall on Mercury Distribution in the Soil (Batch 1)

Mercury concentrations in the soil prior to and after the addition of 3 L of water are shown in Table 16. The dry soil samples were collected before the addition of 3L of water and the moist soil was collected after adding 3 L of water.

Table 16. Effect of single large rainfall for Batch 1.

Chamber	Dry Soil (ppb)	After 3 L water (ppb)	Difference (%)
Control Layer 1	29±1	27±2	-6.9
Control Layer 2	25±2	27±1	8
0.05 kg FGD gypsum Layer 1	32±0	30±1	-6.3
0.05 kg FGD gypsum Layer 2	26±1	26±0	0
0.1 kg FGD gypsum Layer 1	39±1	32±1	-17.9
0.1 kg FGD gypsum Layer 2	26±0	26±1	0

The mercury concentration in layer 1 of the 0.1 kg gypsum chamber decreased significantly (18%) after adding 3 L of de-ionized water. There is no obvious mercury concentration change in the layer 2. The mercury concentration in layer 1 of the 0.05kg gypsum chamber decreased similarly as control.

The soil sampling interval was only 48 hours. During these 48 hours, the water effect played a predominant role. Water content and atmospheric oxidants have been reported to contribute to mercury release from FGD gypsum into soils.[29] The decrease in layer 1 may be due to the water effect and thus a single heavy rain contributes to mercury evaporation.

3.2.2 Effect of Multiple Rainfalls on Mercury Distribution in Soil (Batch 2)

The initial and final mercury concentration for different soil depth in moisture study is provided in Table 17.

Table 17. Effect of multiple rainfalls for Batch 2.

Chamber	Irrigation rate (mL/day)	Initial (ppb)	Final (ppb)
Water 1 Layer 1	130	42±1	35±0
Water 1 Layer 2	130	33±2	33±1
Water 2 Layer 1	260	43±0	34±1
Water 2 Layer 2	260	32±0	33±1
Water 3 Layer 1	520	42±1	36±1
Water 3 Layer 2	520	36±1	34±1

Mercury concentration in the topsoil (Layer 1) decreased after six weeks. But there is no obvious mercury increase in the subsoil. Reduction of mercury concentration in water chambers 1 – 3 (Layer 1) was around 15%. Therefore, increasing the irrigation rates has negligible effect on mercury transport in FGD gypsum treated soil, once a saturation level has been attained.

3.2.3 Mercury Concentrations in Different Soil Types

The effect of soil types was shown in Table 18.

Table 18. Mercury concentration (ppb) in different kinds of soil.

Soil types	Layers	Week 1	Week 6	Difference (%)
Clay soil	Layer 1	32±0	26±1	-18.8
	Layer 2	28±0	26±0	-7.1
Organic soil	Layer 1	43±0	32±0	-25.6
	Layer 2	34±1	33±1	-2.9

For this comparison, the only difference is the soil type. In layer 1, both have significant mercury loss. Mercury loss in the organic soil is larger than in the clay soil, indicating that mercury transport is affected by soil types.

3.2.4 Comparison of Bare and Plant Covered Soil

Table 19. Change in mercury concentration after 1 month (bare soil) – Batch 1.

Chamber	Pre-moistened Soil (ppb)	Final (ppb)	Difference (%)
Control Layer 1	27±2	27±1	0
Control Layer 2	27±1	28±1	3.7
0.05 kg Layer 1	30±1	28±0	-6.7
0.05 kg Layer 2	26±0	29±0	11.5
0.1 kg Layer 1	32±1	30±0	-6.2
0.1 kg Layer 2	26±1	30±1	15.4

Table 20. Recombination of Table 10 (Tall Fescue Study) to compare with Table 19.

ID	Week 1 (ppb)	Week 6 (ppb)	Difference (%)
Control Layer 1	24±1	22±0	-8.3
Control Layer 2	28.5±2	26.5±2	-7.0
0.5 kg Layer 1	51±2	43±1	-15.7
0.5 kg Layer 2	27.5±1	26.5±2	-3.6
1 kg Layer 1	71±2	57.5±2	-19.0
1 kg Layer 2	24.5±2	27.5±1	3.7

Several trends are noticeable when re-examining portions of Batch 1 (Table 19) with the Tall Fescue Study (Table 20.) First, the mercury in Layer 2 of Batch 1 (bare soil) increases consistently, as compared with, Layer 2 of the combined Tall Fescue Study, which decreases. This trend is possibly due to the plant uptake of mercury. Two, with increasing amounts of applied gypsum there is a corresponding decrease in Layer 1.

3.3 Cherry Radish Study

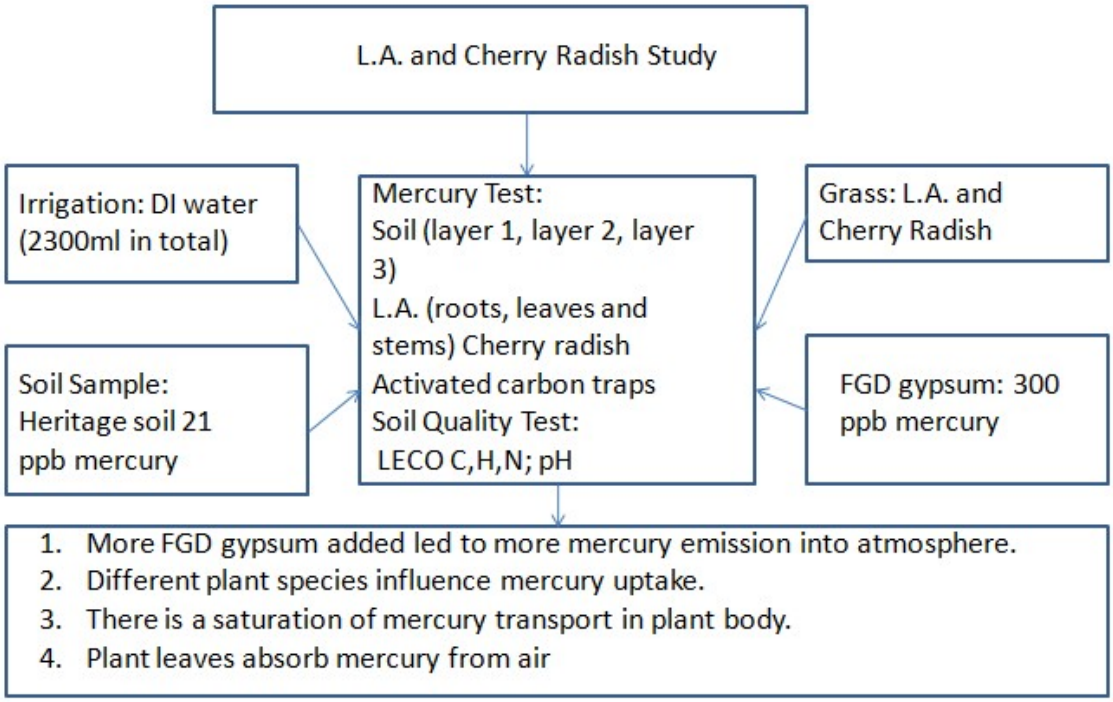


Figure 19. Flow chart of L.A. and cherry radish study.

3.3.1 Soil Mercury Analysis

Table 21. Mercury concentration (ppb) of Layer 1 soil before and after addition.

ID	Control	0.01 kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Before FGD	21±0	21±1	20±0	20±0	22±0	20±0

After FGD	20±0	23±0	26±0	34±0	60±1	97±1

Table 22. Final mercury concentration (ppb) in the soil.

ID	Control	0.01 kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Adjacent	19±0	20±0	25±0	32±0	59±3	89±1
Layer 1	21±0	21±0	23±0	28±1	52±0	77±0
Layer 2	21±0	21±0	21±0	22±0	29±0	32±0
Layer 3	20±0	21±1	20±1	20±0	21±0	20±0

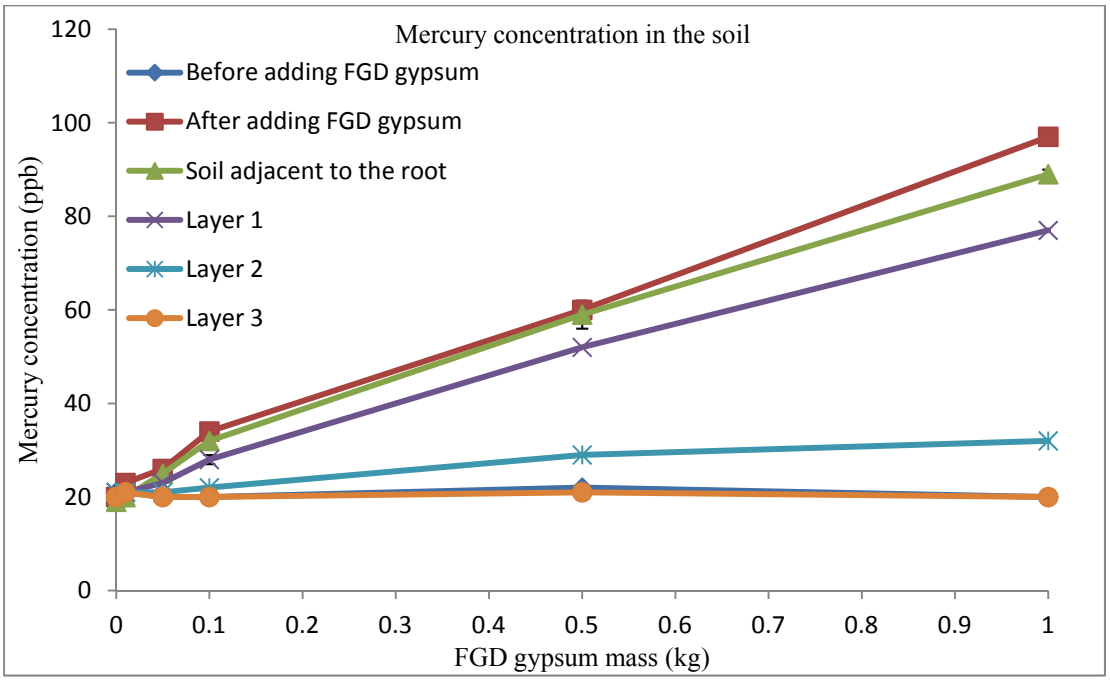


Figure 20. Mercury concentration versus applied FGD gypsum.

Figure 20 shows the mercury concentration before and after adding FGD gypsum and mercury concentration in different layers at the end of this study.

After adding FGD gypsum to the soil, mercury concentration in the soil increased. As more FGD gypsum was added, the mercury concentration increased in the soil. The soil adjacent to the root has a higher mercury concentration than other parts of the surface

soil. Furthermore, the soil adjacent to the root has relatively similar mercury concentration as the beginning of adding FGD gypsum. Mercury showed a tendency to collect around the roots, thus, keeping mercury in the soil.

The mercury concentration of Layer 2 increased at the end of the study. It has been reported that FGD gypsum has good mobility; therefore, it can leach into subsoil through rainfall or irrigation. The mercury in FGD gypsum was transported into the subsoil with the FGD gypsum, and thereby the mercury concentration was higher in Layer 2. However, the mercury concentration of Layer 3 did not increase after FGD gypsum addition, meaning the mercury did not migrate into the bottom soil.

3.3.2 Mercury Emission

Section 1 is the sampling portion. Section 2 provides a breakthrough area for samples where Section 1 is not sufficient for 100% capture of mercury.

Table 23. Mercury mass (ng) and concentration (ng/m^3) in the carbon traps.

ID	Control	0.01 kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Section 1	18	30	455	701	926	1541
Section 2	1	0	14	8	2	50
Total	19	30	469	709	928	1591
Concentration (ng/m^3)	0.1	0.1	2.0	3.0	4.0	7.0

The flow rate of the air out was 0.3 m^3/ hour, and the experimental time was 33 days. The mercury concentration was calculated by the equation [9]:

$$[9] \quad \text{Mercury Concentration} = \frac{M_{Hg}}{V \times T}$$

Where M_{Hg} is the sum of mercury mass collected from section 1 and section 2 of activated carbon trap. V is the flow rate of the air out. T is time. For example, in control

chamber: flow rate is 0.3 m^3/hour × 33 days × 24 hours = 238 m^3. The mercury concentration in the air was calculated as: 19 ng/238 m^3 = 0.1 ng/m^3.

As more FGD gypsum was applied to each chamber, mercury emission increased. Section 2 had low mercury mass, which means there was near zero breakthrough of the carbon trap.

As more FGD gypsum was added, consequently more mercury was added into each chamber, resulting in more mercury available for conversion to elemental or methylated forms.

In addition, one possible reason for the increase is that mercury species in FGD gypsum was in ionic form[30], and therefore, is able to dissolve in the water. Utilizing water evaporation as a mode of transportation, mercury was released from the soil. With the increased addition of FGD gypsum, more mercury was dissolved in the water, and thereby more mercury evaporated into the atmosphere, which is in good agreement with the results of the moisture study.

3.3.3 Plants Mercury Analysis

Table 24 reveals the mercury concentration in the lamium amplexicaule (L.A.) root, leaves and stems, and mercury concentration in the cherry radish root and leaves/stems.

Table 24. Lamium amplexicaule (L.A.) and cherry radish mercury concentration (ppb).

ID	L.A. Root	L.A. Leaves	L.A. Stems	Radish Root	Radish Leaves and stems
Control	15±0	10±2	9±1	N.A.	N.A.
0.01kg	20±0	17±1	17±2	26±2	65±6
0.05 kg	25±4	18±3	33±4	33±0	54±5
0.1 kg	46±0	27±3	51±6	38±3	56±5
0.5 kg	41±1	26±3	24±3	39±0	20±0
1 kg	113±0	54±3	54±4	58±3	45±3

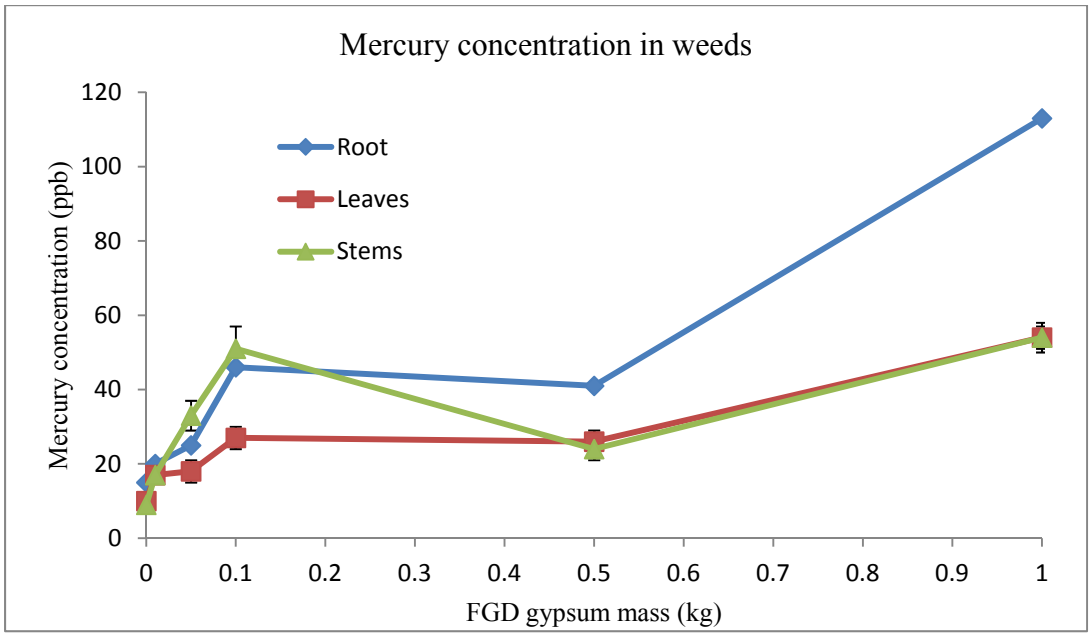


Figure 21. Mercury distribution in lamium amplexicaule.

The mercury concentration in the plants increased after addition of FGD gypsum. Plants absorb metal elements according to elemental size and valence state. Plants may absorb mercury because the mercury size and valence state is similar to plant nutrients.

The mercury concentration in lamium amplexicaule leaves and roots increased as more FGD gypsum was added. The seeds of lamium amplexicaule are at the top of the plant, meaning all the nutrition is transported from the roots to the top part with the stem serving as the transportation pathway. The mercury concentration of the stem did not increase after the 0.1 kg addition, meaning that is a saturation level has been attained. Thus, the stems were not able to transport mercury from the roots to the leaves. However, the mercury concentration in the leaves still increased after 0.1 kg addition, meaning the leaves must have absorbed this mercury from the air.

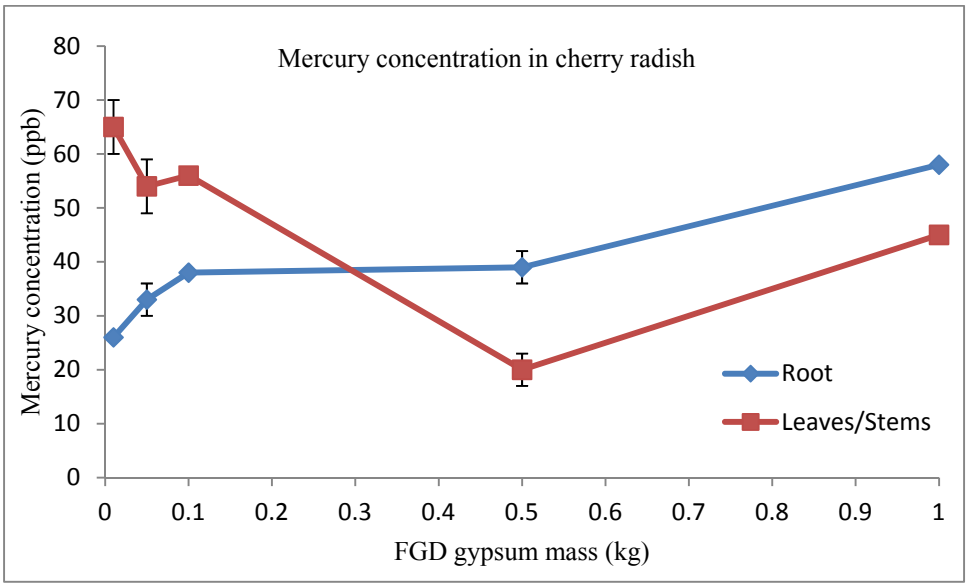


Figure 22. Cherry radish mercury distribution.

Mercury concentration in the cherry radish root increased with increasing FGD gypsum mass, but the mercury concentration in the leaves and stems varied. The variation may be due to a blocking effect by mercury in the transport system of the plant. Cherry radish was located under the soil rather than on the top of plants, so all the nutrients were transported from top to the bottom. Mercury transportation in the plant leads to varying mercury distribution in the cherry radish.

3.3.4 Cherry Radish Mass Balance

Mercury concentration of FGD gypsum is 300 ppb, and the initial mercury concentration in the soil is 21 ppb, the mercury concentration of seed and de-ionized water is below the detection limit.

Therefore, at initial conditions:

The mass of mercury upon the gypsum application was calculated according to equation [10]:

$$[10] \quad \text{Mercury Mass} = M_{soil} \times C_{soil} + M_{gypsum} \times C_{gypsum}$$

In 0.05 kg FGD gypsum application rat, the mass of mercury in soil:

$$10\ \text{kg} \times 21 \times 10^{-9} + 0.05\ \text{kg} \times 300 \times 10^{-9} = 225{,}000\ \text{ng}$$

Table 25. Initial mercury mass (ng).

ID	Control	0.01 Kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Mercury mass	210000	213000	225000	240000	360000	510000

Final condition (After test during 33 days of growth of plant):

Mercury mass in soil:

Table 26. Final mercury mass (ng).

ID	Control	0.01 Kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Layer 1	73500	73500	80500	9800	182000	269500
Layer 2	73500	73500	73500	77000	101500	112000
Layer 3	60000	63000	60000	60000	63000	60000
Total	207000	210000	214000	235000	346500	441500

The mass of mercury upon the gypsum application was calculated by the equation [11]:

$$[11] \quad \text{Mercury Mass} = \sum_{i=1}^{3} M_{soil} \times C_{soil}$$

In the 1 kg FGD batch, the mass of mercury in soil:

$$3.4 \text{ kg} \times 77 \times 10^{-9} + 3.5 \text{ kg} \times 32 \times 10^{-9} + 3 \text{ kg} \times 20 \times 10^{-9} = 441500 \text{ ng}$$

Table 27. Final L.A. and cherry radish mercury concentration (ppb) versus applied FGD gypsum.

Plant type	Control	0.01 kg	0.05kg	0.1kg	0.5kg	1kg
L.A.	11	18	30	45	31	61
Cherry radish	0	71	53	52	33	45

Lamium amplexicaule and radish mercury concentration were calculated from equation [12]:

$$[12] \quad \text{Mercury Concentration} = \frac{\sum_{i=1}^{n} X_i Y_i}{\sum_{i=1}^{n} X_i}$$

X_i represents the mass of each part of the sample; Y_i represents the corresponding mercury concentration for that part of the sample.

Table 28. Final L.A. and cherry radish mercury mass (μg) versus FGD gypsum mass.

Plant type	Control	0.01 kg	0.05 kg	0.1 kg	0.5 kg	1 kg
L.A.	24	27	77	150	63	66
Cherry radish	0	11	22	68	6	67
Total mass	24	138	99	218	69	133

Calculation procedure:

For the 1 kg FGD batch, the mass of mercury in the plant:

$$61 \times 10^{-9} \times 1.079 \text{ g} + 33 \times 10^{-9} \times 2.03 \text{g} = 133 \text{ ng}$$

Table 29. Mercury mass (ng) in the activated carbon traps versus FGD mass.

ID	Control	0.01 kg	0.05 kg	0.1 kg	0.5 kg	1 kg
Section 1	18	30	455	701	926	1541
Section 2	1	0	14	8	2	50
Total	19	30	469	709	928	1591

The total mercury mass balance was shown in Table 30.

Table 30. Mercury recovery in cherry radish study versus applied FGD gypsum.

I.D.	Grass (ng)	Soil Mixture (ng)	Carbon Trap (ng)	Infiltrated Water (ng)	Final Mercury (ng)	Initial Mercury (ng)	Recovery (%)
Control	24	207000	19	N.D.	207043	210000	99
0.01kg	138	210000	30	N.D.	210168	213000	99
0.05kg	99	214000	469	N.D.	214568	225000	95
0.1 kg	218	235000	709	N.D.	235927	240000	98
0.5 kg	69	346500	928	N.D.	347497	360000	97
1kg	133	441500	1591	N.D.	443224	510000	87

Soil Quality Analysis

3.3.5 C, H, N analysis

Table 31. Carbon, nitrogen, and hydrogen content in soil after adding FGD gypsum.

ID	Carbon (%)	Nitrogen (%)	Hydrogen (%)
Control	2.0±0.1	0.6±0.0	0.7±0.0
0.01 kg FGD	2.1±0.1	0.7±0.0	0.7±0.0
0.05 kg FGD	2.2±0.1	0.8±0.0	0.8±0.0
0.1 kg FGD	2.1±0.1	0.7±0.0	0.7±0.0
0.5 kg FGD	1.9±0.1	0.9±0.0	0.9±0.0
1 kg FGD	2.0±0.1	1.1±0.0	1.1±0.0

The application of FGD gypsum did not noticeably change carbon, hydrogen, nitrogen concentrations in the soil.

3.3.6 pH Value

Table 32. Comparison of pH values before and after adding FGD gypsum.

ID	Before adding FGD gypsum	After adding FGD gypsum	Increased (%)
Control	5.0±0.0	5.0±0.0	0.0
0.01 Kg	5.0±0.0	5.0±0.0	0.0
0.05 kg	5.0±0.0	5.1±0.0	2.0
0.1 kg	5.3±0.0	5.3±0.0	0
0.5 kg	5.2±0.0	5.8±0.0	11.5
1 kg	5.1±0.0	6.6±0.0	28.9

When small amounts of FGD gypsum were added to the chamber, the pH was only minimally affected. After the addition of 0.5 kg and 1 kg FGD gypsum, soil pH increased by 11.5% and 28.9%. Definitely, FGD gypsum did not affect soil pH as much as lime. The major constituent for limestone is $CaCO_3$, which reacts with clay in the soil to form H_2CO_3, and thereby produce CO_2 and H_2O. This means limestone can change the H^+ concentration in the soil. The major constituent for FGD gypsum is $CaSO_4$, which reacts with clay in the soil form H_2SO_4, which has been shown in equations [13] and [14]. FGD gypsum only affected the H+ concentration in the soil at massive doses, which is most probably due to unreacted $CaCO_3$ in the FGD gypsum.

$$[13]\ CaCO_3 + Soil \rightarrow Soil - Ca^{2+} + HCO_3^- \rightarrow Soil - Ca^{2+} + H_2O + CO_2$$

$$[14]\ CaSO_4 + Soil \rightarrow Soil - Ca^{2+} + HSO_4^-$$

FGD gypsum can offset the disadvantages of acidic soil. The soil used in the greenhouse is definitely acidic due to its low pH value. In acidic conditions, aluminum is a concern; the calcium in FGD gypsum displaces the aluminum, allowing the sulfate ion to bond with aluminum, which is a more easily dissolved and thus able to migrate to greater soil depths. The reaction is shown in equation [15].[31, 32]

$$[15]\ CaSO_4 + Al^{3+} \rightarrow Al(SO_4)^+ + Ca^{2+}$$

3.4 Field Study

Table 33. Corn Harvest Mass.

Gypsum type	Run 1	Run 2	Run 3
Control	16	10	11
Mined gypsum	11	9	12
FGD gypsum	10	11	26

There are 12 rows in a given plot. Three rows of corn (the middle rows) were collected at the end of the study. Since Control 1 and FGD 3 plots were twice as large as the other plots, the total mass was divided by 2.

For the Control plot, the total yield mass is:

$$(16/2 + 10 + 11)/3 \text{ rows} \times 12 \text{ rows} = 116 \text{ kg}$$

For the Mined gypsum plot:

$$(10 + 9 + 11)/3 \text{ rows} \times 12 \text{ rows} = 120 \text{ kg}$$

For the FGD gypsum plot:

$$(11 + 12 + 26/2)/3 \text{ rows} \times 12 \text{ rows} = 144 \text{ kg}$$

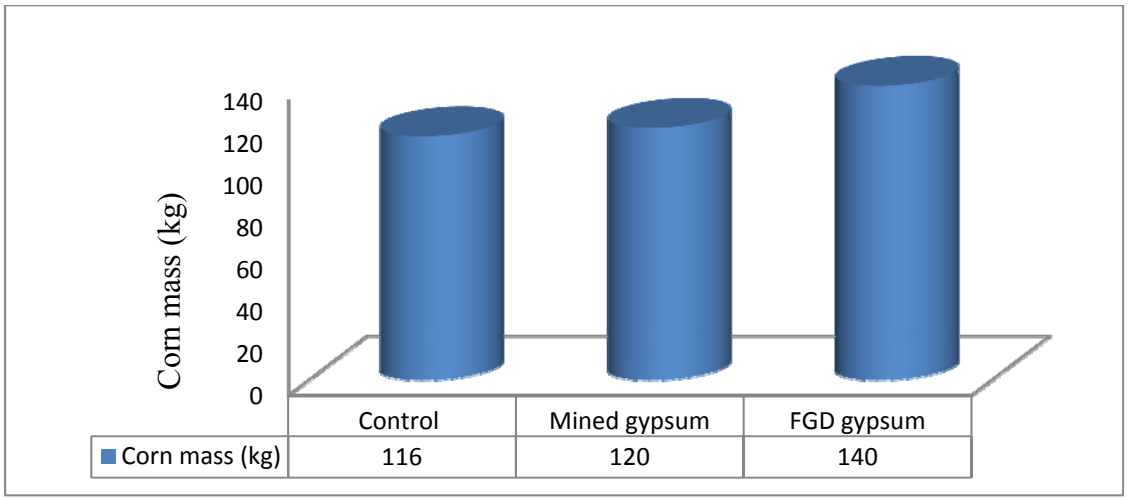


Figure 23. Corn plots yield data.

FGD gypsum appeared to promote plant growth, by increasing corn yield by 21%.

Table 34. Mercury concentration in corn.

Gypsum type	Whole Stalk (ppb)	Kernel (ppb)
Control	12±6	25±2
Mined gypsum	26±3	25±1
FGD gypsum	35±1	22±3

In this field study, the FGD gypsum used had the same mercury concentration as that of mined gypsum. The mercury concentration of the whole stalk was higher in FGD gypsum plots than the mined gypsum plots. The FGD gypsum mercury may be more easily absorbed by the plant than the mined gypsum.

The mercury concentration of the corn kernels from the FGD gypsum, mined gypsum and control plots are all similar.

Table 35. Mercury mass of activated carbon trap in June.

Height (cm)	Control (ng)	FGD (ng)
Trap 1 (0-15)	21	18
Trap 2 (15-30)	20	9
Trap 3 (30-45)	19	20
Trap 4 (45-60)	19	17
Trap 5 (60-75)	18	18
Trap 6 (75-90)	20	15
Total (ng)	117	97
Concentration (ng/m^3)	1.6	1.3

The vacuum pump flow rate was $0.3m^3$/hour, and the pump pulled air through the traps for ten days, so the total air volume was:

$0.3\ m^3/hour \times 10\ days \times 24\ hours = 72\ m^3$

There was no definitive mercury trend for the carbon traps in both the control plot and FGD plot. Mercury emission of the FGD gypsum plot was similar to the control plots in June and August.

Table 36. Activated Carbon Traps in August.

Height (cm)	Control (ng)	FGD (ng)
Trap 1 (0-15)	37	45
Trap 2 (15-30)	47	43
Trap 3 (30-45)	37	35
Trap 4 (45-60)	39	33
Trap 5 (60-75)	34	32
Trap 6 (75-90)	27	37
Total (ng)	221	225
Concentration (ng/m^3)	3.1	3.1

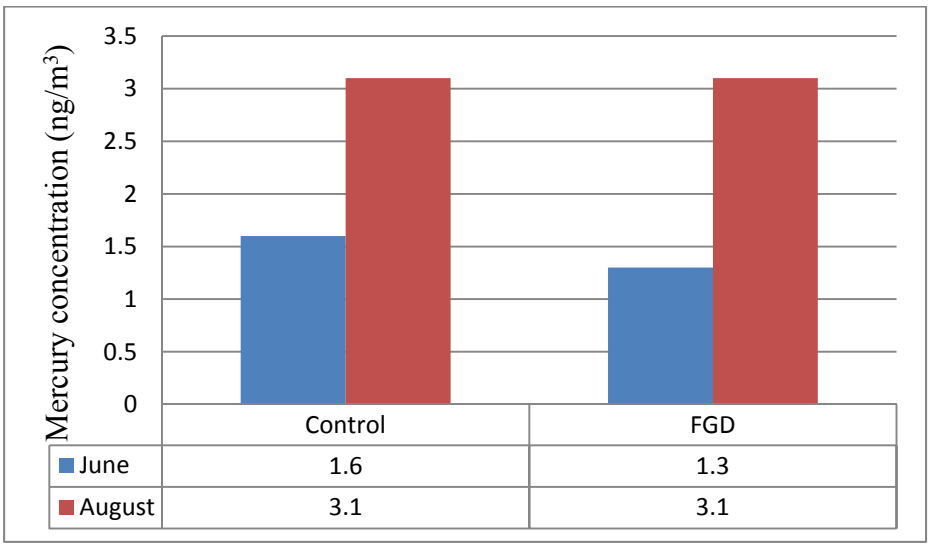


Figure 24. Mercury emission concentration in June and August.

For the August FGD plot, mercury emission near the ground was higher than the emission at the top. Mercury emission of the FGD plot was similar to the control. Mercury emission in both of the August plots was higher than June. In June 2011, the average temperature was 23℃, whereas the average temperature in August was 24℃. The month of June had 87 mm of rain. The month of August had 175 mm of rain. Higher temperatures and higher precipitation resulted in more mercury evaporation in the field study.

4. Conclusions

4.1 Effect of FGD Gypsum on Corn Yield

A field study indicated that both FGD gypsum and mined gypsum can positively increase plant growth and the corn yield by about15% to 23%.

4.2 Mercury Evaporation

A field study indicates that mercury evaporation was likely enhanced from gypsum amended soil by elevated temperature and increased rainfall. This has been evidenced by increased mercury transformation into the atmosphere in August than in June when lower temperatures and less rainfall were typical.

In the cherry radish study, analysis of activated carbon traps showed that increased mercury emission into the atmosphere resulted from increased FGD gypsum application, evidenced by direct sampling of mercury based EPA 30B method.

In the moisture study, a single heavy rainfall was attributed to increased mercury emission in the greenhouse study.

4.3 Mercury Uptake

The results from studies of both fescue and cherry radish indicated that mercury uptakes increased up to a certain amount with increasing FGD gypsum. After the saturation level was reached, additional increases in FGD gypsum did not result in an increase in mercury uptakes by the plants. It appears that non-food plants could assist in keeping mercury in the soil and prevent the evaporation of mercury into the atmosphere, as well as, infiltration into the ground water. This is in agreement to Millhollen's conclusion that mercury accumulation in plant roots is an important process.[33] The analysis of L.A.'s roots, stems, and leaves show that while roots accumulate mercury, the

stem is not active in the transportation of mercury to the leaves. Thus, the mercury content found in the leaves is most likely from absorption from the air.

4.4 Mercury Infiltration

In the greenhouse study, mercury in gypsum amended soil migrated downward as the irrigation water was applied, however, the mercury was absorbed and did not follow water all the way into the underground water collection. The irrigated water carried soluble mercury from the topsoil to sub-surface soil.

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ACHIEVEMENTS

Presentation:

1. Kelin Wang, Ying Wen, Yan Cao, Wei-Ping Pan. "Minimizing Toxicity of Coal Combustion By-Products by Oxalate". The 96th Kentucky Academic Science Annual Meeting, Western Kentucky University, Bowing Green, KY, November 13th, 2010
2. Kelin Wang, William Orndorff, Yan Cao, Wei-ping Pan. Studies of Soil Amendment Using Flue Gas Desulfurization (FGD) Gypsum in Greenhouse. 42nd Anuual WKU Student Research Conference, Western Kentucky University, Bowling Green, KY, March 26th, 2011
3. Kelin Wang, William Orndorff, Yan Cao, Wei-Pan. Greenhouse and Field Studies of Flue Gas Desulphurization By-Products Amended Soil. The 97th Kentucky Academic Science Annual Meeting, Murray State University, Murray, KY, November 04. 2011
4. Kelin Wang, William Orndorff, Yan Cao, Wei-Ping Pan. Fate of Mercury in Flue Gas Desulphurization Gypsum Amended Soil. 42nd Anuual WKU Student Research Conference, Western Kentucky University, Bowling Green, KY, March 24th, 2012
5. Kelin Wang, William Orndorff, Yan Cao, Wei-Ping Pan. Fate of Mercury in Flue Gas Desulphurization Gypsum Amended Soil. ACS 243rd National Meeting. San Diego California. March 27th, 2012

Publication:

1. Kelin Wang, William Orndorff, Yan Cao, Wei-Ping Pan. In-house Greenhouse Investigation of Transformation of Trace Elements in FGD Gypsum Amended Soil. *Preprint of Symposia-American Chemical Society. Fuel Chemistry.* **2011**. 56 (2), 40-41

2. Kelin Wang, William Orndorff, Yan Cao, Wei-Ping Pan. Greenhouse and Field Studies of Flue Gas Desulphurization By-Products Amended Soil. *Preprint of Symposia-American Chemical Society. Fuel Chemistry.* **2012**
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